



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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|--|--------------------------|--|---|
| (51) International Patent Classification <sup>6</sup> :<br><b>A61K 7/043</b>   |                          | <b>A1</b>  | (11) International Publication Number: <b>WO 99/55291</b>   |
|  |                          |  | (43) International Publication Date: 4 November 1999 (04.11.99)   |
| (21) International Application Number: <b>PCT/IB99/00646</b>   |                          | (74) Agents: REED, T., David et al., The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US). |   |
| (22) International Filing Date: 12 April 1999 (12.04.99)   |                          |  |   |
| (30) Priority Data:<br>60/083,020  | 24 April 1998 (24.04.98) | US   | (81) Designated States: AU, CA, CN, CZ, CZ (Utility model), JP, KR, MX, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). |
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| (54) Title: NAIL POLISH COMPOSITIONS   |                          |  |   |
| (57) Abstract  |                          |  |   |
| <p>The present invention relates to compositions which are useful as cosmetic or therapeutic agents for nails. The present compositions form films exhibiting a Surface Energy of at least 42.5 mJ/m<sup>2</sup> (e.g., 42.5 to 43.5), preferably greater than 43.5 mJ/m<sup>2</sup>. The compositions alternatively or additionally advantageously provide films having a Polarity of from 0.24 to about 0.31. The compositions and films are particularly useful as nail polishes providing improved wear. Preferred compositions contain, by weight of the composition, from about 5 % to about 20 % of a film forming cellulosic polymer, from about 1.25 % to about 8 %, of a film forming polyurethane polymer, from about 3 % to about 20 % of a plasticizer, and from about 55 % to about 90 % of a volatile, organic solvent. The invention also relates to films formed from the compositions, and methods of treating the nails comprising application of the composition to the nails.</p> |                          |  |   |

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## NAIL POLISH COMPOSITIONS

### TECHNICAL FIELD

The present invention relates to compositions suitable for cosmetic and/or  
5 therapeutic treatment of the nails, e.g., nail polishes. The compositions provide films having defined Surface Energy and/or Polarity, and exhibiting improved wear.

### BACKGROUND OF THE INVENTION

Consumers use nail polishes to cosmetically enhance their nails or protect the  
nails from everyday conditions and stressors. However, the nail polishes of which  
10 the present inventors are aware are deficient in many respects, including their inability to provide long wear. Such nail polishes often exhibit deterioration, particularly in the form of chipping or peeling, in as few as one or two days. Such deterioration is exhibited primarily at the tip of the nail. The occurrence of this deterioration often forces consumers to remove their nail polish soon after original  
15 application and reapply additional nail polish to the nails. Consumers may also attempt to correct the unsightly appearance of the deteriorating nail polish by "touching-up" the areas of the nail which exhibit the deterioration, a practice which actually impairs the overall look of the nail polish. Finally, consumers may choose to do nothing about the deterioration and allow, for example, chipping and peeling to  
20 progress, resulting in nails which are not only minimally protected from the environment but are unsightly as well.

Extreme examples of nail polish compositions which exhibit inadequate wear are those which are easily and completely peeled or stripped off the nails without the use of a solvent. Other nail polish compositions are completely removable with  
25 water and, therefore, are not practical for normal use and do not provide long wear under everyday conditions.

The art is replete with nail polish compositions which are promoted as having long wear, good adhesion, and/or resistance to chipping. While some nail polish compositions provide better wear than others, a need remains for nail polishes  
30 which provide improved wear. It would therefore be desirable to provide nail polish

compositions having improved wear properties including, for example, improved adhesion to the nail.

It has been surprisingly discovered that nail polishes exhibiting Surface Energies and/or Polarities over defined ranges, as described herein, provide enhanced adhesion of nail polish to the nail. The present inventors have further discovered nail polish compositions which form films which provide these properties. The present compositions provide nail polish films exhibiting wear at a superior level to nail polishes of which the present inventors are aware.

### SUMMARY OF THE INVENTION

The present invention relates to compositions suitable for application to the nails, e.g., as a nail polish, which provide films exhibiting defined surface properties, namely Surface Energies and/or Polarities. The films having these properties exhibit improved wear.

Compositions having these properties preferably comprise:

- a) from about 5% to about 20%, by weight of the composition, of film forming cellulosic polymer;
- b) from about 1.25% to about 8%, by weight of the composition, of film forming polyurethane polymer;
- c) from about 3% to about 20%, by weight of the composition, of plasticizer; and
- d) from about 55% to about 90%, by weight of the composition, of volatile, organic solvent.

The compositions advantageously provide films having a Surface Energy of at least 42.5 mJ/m<sup>2</sup> (e.g., 42.5 to 43.5), preferably greater than 43.5 mJ/m<sup>2</sup>. The compositions alternatively or additionally advantageously provide films having a Polarity of from about 0.24 to about 0.31.

The invention also relates to films formed from the compositions, and methods of treating the nails comprising application of the composition to the nails.

### DETAILED DESCRIPTION OF THE INVENTION

The essential components of the present invention are herein described below. Also included are non-limiting descriptions of various optional and preferred components useful in the compositions of the present invention.

The present invention can comprise, consist of, or consist essentially of any of the required or optional components and/or limitations described herein.

In the description of the invention various embodiments and/or individual features are disclosed. As will be apparent for the skilled practitioner all combinations of such embodiments and features are possible and can result in preferred executions of the invention.

All percentages and ratios are calculated by weight unless otherwise indicated. All percentages are calculated based on the total composition unless otherwise indicated.

All component or composition levels are in reference to the active level of that component or composition, and are exclusive of impurities, for example, residual solvents or by-products, which may be present in commercially available sources.

Referred to herein are trade names for materials including, but not limited to, polymers and optional components. The inventors herein do not intend to be limited by materials under a certain trade name. Equivalent materials (e.g., those obtained from a different source under a different name or catalog (reference) number) to those referenced by trade name may be substituted and utilized in the compositions herein.

Active and other ingredients useful herein may be categorized or described herein by their cosmetic and/or therapeutic benefit or their postulated mode of action. It is to be understood that the active and other ingredients useful herein can in some instances provide more than one cosmetic and/or therapeutic benefit or operate via more than one mode of action. Therefore, classifications herein are made for the sake of convenience and are not intended to limit an ingredient to the particularly stated application or applications listed.

All documents referred to herein, including all patents, patent applications, and printed publications, are hereby incorporated by reference in their entirety.

The compositions of the present invention are suitable for application to animal nails, including human nails. The compositions of the present invention are useful, for example, for providing aesthetic, cosmetic, therapeutic, and/or prophylactic benefits to the nails. As used herein, the term "nail polish" is a

comprehensive term describing a nail polish composition, product (including coloring products), or the like, which is useful for providing, for example, aesthetic, cosmetic, therapeutic, and/or prophylactic benefits to the nails.

As used herein, the term "animal nail" means a keratinaceous plate present at the upper surface of the end of a finger or toe of a primate or the analogous claw, hoof or the like of other animals.

As used herein, the term "suitable for application to animal nails" means that the compositions are suitable for use in contact with animal nails without undue toxicity, incompatibility, instability, allergic response, and the like in regard to a given animal species. Preferred compositions are those suitable for application to human nails.

In addition to natural nails, the compositions herein may also be used for application to synthetic (artificial) nails.

Film-forming polymers (a) and (b)

The present compositions comprise one or more film-forming, solvent-borne, cellulosic polymers and polyurethane polymers.

The film-forming polymers herein are solvent-borne polymers. As used herein, the term "solvent-borne", with reference to a film-forming polymer, means that the polymer was prepared under substantially anhydrous conditions and is preferably added to the composition which it comprises as a substantially anhydrous solution (or other mixture, whether heterogeneous or homogeneous, preferably homogeneous). As used in reference to a composition suitable for application to the nails, a solvent-borne composition means that the composition comprises one or more organic solvents and is substantially anhydrous, preferably comprising less than 2% water, more preferably less than 1% water, most preferably less than 0.25% water. Solvent-borne polymers and compositions are preferred.

The term "film-forming polymer" means a homopolymer, copolymer, or mixture thereof which, as recognized in the polymer arts, forms an adherent continuum from a composition when applied to a substrate (in the present invention, nails). See, e.g., *Polymer Colloids*, Robert M. Fitch, ed., New York: Plenum Press, pp. 173-183 (1971). As used herein, the term "copolymer" includes linear, block, branched, graft, comb, and star copolymers. The film-forming polymers useful

herein are self-curing polymers. That is, they do not require chemical reaction or introduction of energy (e.g., exposure to ultraviolet rays) to form the adherent continuum.

The film-forming polymers herein can be selected from nonionic, ionic  
5 (anionic or cationic), and amphoteric (including zwitterionic) polymers.

The film-forming cellulosic polymers may be selected from polymers derived from cellulose such as are known in the art, including but not limited to cellulose esters. Preferred cellulosic polymers are nitrocellulose, nitrocellulose esters such as cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, and  
10 mixtures thereof. More preferred are nitrocellulose, cellulose acetate butyrate, cellulose acetate propionate, and mixtures thereof. Nitrocellulose polymers are most preferred. Exemplary nitrocellulose polymers are nitrocellulose RS types (nitrogen content of 11.5-12.2%) of Hercules, such as nitrocellulose - RS ½ second, - RS ¼ second, - RS 1/8 second, - RS 1/16 second or the like.

15 The compositions hereof preferably comprise a total of from about 5% to about 20%, more preferably from about 6% to about 20%, even more preferably from about 10% to about 17%, most preferably from about 13% to about 16%, cellulosic polymer.

The present compositions also comprise a film-forming polyurethane.  
20 Preferred polyurethanes are selected from aromatic polyether polyurethanes, aliphatic polyether polyurethanes, aromatic polyester polyurethanes, aliphatic polyester polyurethanes, aromatic polycaprolactam polyurethanes, aliphatic polycaprolactam polyurethanes, urethane acryl copolymers, siloxane-urethane copolymers, and mixtures thereof. More preferred are aromatic polyether  
25 polyurethanes, aliphatic polyether polyurethanes, aromatic polyester polyurethanes, aliphatic polyester polyurethanes, aromatic polycaprolactam polyurethanes, aliphatic polycaprolactam polyurethanes, and mixtures thereof. Aromatic polyether polyurethanes, aliphatic polyether polyurethanes, aromatic polyester polyurethanes, aliphatic polyester polyurethanes and mixtures thereof are even more preferred.  
30 Aliphatic polyether polyurethanes, aliphatic polyester polyurethanes, and mixtures thereof are most preferred.

Preferred solvent-borne polyurethanes include Sanres EX519\*, Sanres EX499\* (hexylene glycol/neopentyl glycol/TPDI [isophorone diisocyanate] copolymer), Sanres 12711\*, Sanres 6010\*, and Sanres 6012\* (all of which are available from B.F. Goodrich). The most preferred polyurethane is Sanres EX519\*.

Preferred polyurethanes are those having a number average molecular weight of from about 10,000 to about 80,000, more preferably from about 15,000 to about 50,000, most preferably from about 20,000 to about 35,000.

The present compositions preferably comprise a total of at least about 1.25% film forming polyurethane, e.g., at least about 2%, 3%, 3.5% or 5% film-forming polyurethane. The present compositions preferably comprise a total of from about 1.25% to about 8%, more preferably from about 1.5% to about 5%, most preferably from about 2% to about 4%, film-forming polyurethane.

#### Plasticizers (c)

The compositions hereof further comprise one or more plasticizers such as are known in the art. The plasticizer is generally used in an amount to plasticize the film forming polymers so that the nail polish has acceptable flexibility on the nail. The compositions preferably comprise from about 3% to about 20%, more preferably from about 5% to about 20%, even more preferably from about 6% to about 15%, most preferably from about 6% to about 10%, plasticizer.

Preferred plasticizer systems are those which reduce brittleness and increase toughness of the nail polish films and which do not inordinately increase viscosity of the nail polish at the level used.

Preferred plasticizers are selected from the group consisting of polar plasticizers comprising epoxy linkages, linkages comprising a nitrogen atom such as amide, imide, urea and/or urethane linkages, including polar resin plasticizers comprising the foregoing linkages, polyesters, polyester acids (e.g., di- and tri-acids), phthalates, camphor and mixtures thereof. The compositions hereof preferably comprise a plasticizer selected from the group consisting of polar plasticizers comprising amide linkages, polyesters, polyester acids, and mixtures thereof.

Nonlimiting examples of suitable plasticizers are alkyl toluene-sulfonamides, e.g., ethyl toluene-sulfonamide (e.g., Uniplex PX-45 commercially available from

Unitex Chemical Corp. of Greensboro, NC), ; toluene-sulfonamide formaldehyde ("TSF"); polyesters, e.g., Uniplex 670P (commercially available from Unitex Chemical Corp. of Greensboro, NC); polyester acids, e.g., C<sub>3</sub>-C<sub>20</sub>, preferably C<sub>4</sub>-C<sub>12</sub>, more preferably C<sub>6</sub>-C<sub>10</sub> polyester acids (including di- and tri-acids), such as polyester  
5 sebacates (e.g., Paraplex G-25<sup>®</sup>, commercially available from C.P. Hall, Bedford Park, IL) and polyester adipates (e.g., Paraplex G-50<sup>®</sup>, commercially available from C.P. Hall); those disclosed in WO 97/00664, Chen et al, assigned to Eastman Chemical Co; phthalates, e.g., diethyl phthalate, dibutyl phthalate, and dioctyl phthalate; nonionic surfactant polymers, e.g., tartrates, (e.g., diethyl tartrate, and  
10 dibutyl tartrate, phosphates (e.g., diethyl phosphate and dibutyl phosphate) and glycols (e.g., tetraethylene glycol di-2-ethylhexoate, commercially available from C.P. Hall as Tegmer<sup>®</sup>); camphor; sucrose acetate isobutyrate; and castor oil.

Preferred plasticizers have a number average Molecular Weight of about 10,000 or less. Preferred compositions are essentially free of, and preferably  
15 contain no formaldehyde resins.

Plasticizer mixtures comprising at least one alkyl toluene-sulfonamide (e.g., C<sub>1</sub>-C<sub>10</sub>, preferably C<sub>2</sub>-C<sub>4</sub> alkyl toluene-sulfonamides) are preferred. A blend of ethyl toluene-sulfonamide and at least one other plasticizer is most preferred. Preferred compositions comprise from about 3% to about 8% (more preferably from about 4%  
20 to about 7%, most preferably from about 4% to about 6%) alkyl toluene-sulfonamide and a total of from about 0.1% to about 6% (more preferably from about 1% to about 5%, most preferably from about 2% to about 3%) of one or more other plasticizers. Preferred other plasticizers are polyesters, polyester acids, camphor, phthalates, and mixtures thereof.

Particularly preferred compositions comprise a plasticizer selected from the group consisting of polyesters, polyester acids, and mixtures thereof, more preferably selected from the group consisting of polyester acids. Polyester adipates are preferred polyester acids. Such plasticizers are preferably used in an amount of from 0.1% to about 6%, more preferably from about 1% to about 5%, most  
30 preferably from about 2% to about 3%.

#### Carrier (d)

The compositions of the present invention further comprise a carrier comprising a liquid diluent. Suitable diluent systems are those which solubilize (i.e., dissolve) the polymers and dry in a reasonable time on nails. The liquid diluent comprises one or more volatile, organic solvents.

5 Preferred volatile organic solvents have a boiling point at 1atm of from about 50 °C to about 140 °C, more preferably from about 56 °C to about 125 °C. Preferred organic solvents are selected from alcohols, esters, ketones, aromatic hydrocarbons, aliphatic hydrocarbons, ethers, and mixtures thereof (more preferably C<sub>1</sub>-C<sub>10</sub>, most preferably C<sub>2</sub>-C<sub>4</sub>). Alcohols and esters are more preferred, esters being most  
10 preferred. Preferred alcohols are monohydric. Preferred monohydric alcohols are ethanol, *iso*-propanol, and *n*-propanol. Preferred esters are butyl-, ethyl-, isopropyl- and propyl-acetate, and mixtures thereof. More preferred esters are ethyl acetate, butyl acetate, isopropyl acetate, and mixtures thereof. Other non-limiting examples of suitable organic solvents are benzyl alcohol, amyl acetate, acetone, heptane, *iso*-  
15 butyl acetate, toluene, methyl acetate, *iso*-butanol, *n*-amyl alcohol, *n*-butyl alcohol, hexane, and methyl ethyl ketone.

The present compositions preferably comprise from about 55% to about 90%, more preferably from about 62% to about 78%, most preferably from about 66% to about 74%, volatile, organic solvent.

#### 20 Optional Components

The compositions of the present invention may additionally comprise optional components such as are known in the art to enhance their performance as a nail polish. For example, antifoams, buffers, chelating agents, coalescents, dispersing agents, dyes, epoxies, fillers, pigments, preservatives, resins, other film  
25 forming polymers, therapeutic and/or prophylactic agents, thickeners, wax additives, wetting agents, and the like can be included in the compositions herein. Such optional components may be dispersed, solubilized, or otherwise mixed into the composition. These components may be added to the compositions hereof singularly or in admixture provided they do not substantially reduce the wear properties of the  
30 compositions. Non-limiting examples of optional components are given below.

#### Pigments or Dyes

One or more pigments and other suitable coloring agents, such as dyes, may be incorporated into the compositions. Suitable pigments are inorganic or organic pigments known as, for example, the FD&C and D&C colors, lakes, and iron oxides. Such pigments are disclosed in the C.T.F.A. Cosmetic Ingredient Handbook, First Edition, 1988. Organic pigments include, for example, D and C Red, Nos. 10, 11, 12, and 13, D and C Red No. 7, D and C Red Nos. 5 and 6, D and C Red Nos. 30 and 34, lacquers such as D and C Yellow No. 5 and D and C Red No. 2, and guanine. Inorganic pigments include, for example, titanium dioxide, bismuth oxychloride, brown iron oxide, and the red iron oxides.

Preferred compositions comprise from 0% to about 10%, by weight of the composition, of pigment and/or dye. More preferably, the compositions comprise from about 0.1% to about 10%, even more preferably from about 0.25% to about 5%, and most preferably from about 0.5% to about 2%, by weight of the composition, of pigment and/or dye.

#### Preservatives

One or more preservatives such as are known in the art may be added to the present compositions to prevent, inhibit, or retard microbial growth in the composition. Preferred preservatives include benzophenone, methyl paraben, ethyl paraben, propyl paraben, benzyl alcohol, benzoic acid, benzoates, sorbates, sodium dehydroacetate, 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride (which may be obtained commercially as Quaternium-15<sup>®</sup> from Dow Chemical Co., Midland, MI). Benzophenone is preferred.

The compositions preferably comprise from 0% to about 0.1% of preservative.

#### Resins

One or more resins may be added to the present compositions, e.g., to promote adhesion, to strengthen the film forming polymers, and/or to increase gloss. The resins, for example, epoxy resins such as toluene-sulfonamide-epoxy, can also plasticize the composition. Examples of suitable resins include epoxies and polyacrylics including Polytex E75<sup>®</sup> (toluene-sulfonamide-epoxy) and NX-55 (both commercially available from Estron Chemical, Inc., Calvert City, KY). Acryloid

B66® (commercially available from Rohm and Haas, Philadelphia, PA) and Avalure AC315 (commercially available from B. F. Goodrich, Cleveland, OH). Preferred compositions comprise both epoxy and polyacrylic resin. A composition preferably comprises from 0% to about 15%, more preferably from about 0.5% to about 10%,  
5 even more preferably from about 0.5% to about 6%, most preferably from about 1% to about 5%, resin by weight of the composition.

#### Slip Aids

One or more slip aids may be added, e.g., to improve surface friction, water resistance, abrasion resistance, and mechanical properties. Slip aids which may be  
10 used include wax additives including, for example, animal, fossil, vegetable, mineral, or synthetic waxes. Suitable wax additives include beeswax, carob, candelilla, ozocerite, polyethylene waxes, paraffin waxes, polypropylene waxes, polytetrafluoroethylene (commercially available as Teflon® from DuPont, Wilmington, DE), nylons, polyamides, and materials containing silicone such as  
15 dimethicone and copolymers of polyether and polysiloxane.

The present compositions preferably comprise from 0% to about 1%, more preferably from about 0.001% to about 0.50%, and most preferably from about 0.001% to about 0.05% of slip aid.

#### Therapeutic and/or Prophylactic Agents

20 One or more therapeutic and/or prophylactic agents, for example, vitamins, proteins, anti-fungal agents, anti-microbial agents, and sunscreens (including UV-A, UV-B, and broad spectrum solar filters) may be added to the present compositions for the further care and protection of the nails.

#### Stabilizers

25 One or more stabilizers may be added to the compositions herein, e.g., to prevent pigment from settling and to achieve desired application properties. Preferred stabilizers include clays, e.g., organically modified bentonites and hectorites such as stearalkonium bentonite and stearalkonium hectorite (commercially available from Rheox, Inc. of Hightstown, NJ).

30 The present compositions preferably comprise from 0.25% to about 3%, more preferably from about 0.5% to about 2.5%, and even more preferably from about 1% to about 2% of stabilizer, by weight of the composition.

### Other Film-Forming Polymers

The compositions hereof may contain one or more additional film-forming polymers such as are known in the art, e.g., polyacryls, polymethacryls, styrene-acryl copolymers, polystyrenes, polysiloxanes, polyesters, silicone-acryl  
5 copolymers, vinyl acetate polymers, and mixtures thereof. Solvent-borne or water-borne polymers may be used, however solvent-borne polymers are preferred.

The present compositions may contain up to about 10%, e.g., up to about 5% or up to about 4%, of additional film-forming polymer.

### Method of Making and Using

10 The compositions of the present invention can be made using conventional formulation and mixing techniques.

A layer of nail polish may be prepared by standard application of the composition to the nail using a standard brush-applicator as is commonly utilized in the art (or equivalent thereof) and drying, that is, removing sufficient liquid diluent  
15 (through evaporation of volatiles, most preferably at ambient pressures and temperatures), to form a substantially dry layer, i.e., a layer which feels dry, smooth, and not tacky when it is touched with a human fingertip.

One or more layers of the composition may be applied to the nail. Generally from 1-4 layers, and preferably from 1-2 layers, is applied to the nail. Typically, on  
20 each application about 25 mg of the composition is applied per nail and allowed to dry to form a layer about 35 microns thick.

The compositions may be used as a clear coat (non-colored), color coat, basecoat, topcoat, or other coating on the nail. Accordingly, other nail treatment compositions such as are known in the art, including nail polishes, may be applied to  
25 the nail in addition to the compositions hereof. However, the compositions hereof are preferably used as the sole nail polish composition, e.g., as a clear coat or color coat.

The compositions of the present invention may be presented to a user or potential user (hereinafter "users") of the composition in association with  
30 information which informs such users that use of the composition will provide one or more benefits, including, but not limited to, high gloss, good coverage, and/or wear properties such as resistance to chipping, peeling, scratching or denting, and

the like. Such information may also include instructions for use to obtain such benefits, e.g., including the method steps described above. By "in association with information" it is meant that the information is either directly printed on the container for the composition itself (including direct printing on the container per se or indirectly via a label or the like affixed to the container), or presented in a different manner including, but not limited to, a brochure, print advertisement, electronic advertisement and/or other advertisement, so as to communicate the information to a consumer of the composition. Such information may accordingly comprise words, pictures, and the like.

#### Properties of Compositions/Films of the Present Invention

##### & Test Methods

##### Surface Properties

The present compositions provide films having defined surface properties, namely Surface Energies and/or Polarities. Without intending to be bound by theory, it is believed that the films having these Surface Energies and/or Polarities exhibit improved adhesion to the nail, which contributes to improved wear.

It has been found that Surface Energy and Polarity are a function of the type and level of cellulosic polymer, non-epoxy containing plasticizer, and volatile solvent in the composition. Preferred compositions have a Surface Energy and/or Polarity predicted by the following equations:

Surface Energy =  $(-0.49)(\text{wt \% cellulosic polymer}) + (1.12)(\text{wt \% non-epoxy plasticizer}) + (0.62)(\text{wt \% volatile solvent})$

Polarity =  $(-0.0060)(\text{wt \% cellulosic polymer}) + (0.015)(\text{wt \% non-epoxy plasticizer}) + (0.0034)(\text{wt \% volatile solvent})$

The compositions advantageously provide films having a Surface Energy of at least  $42.5 \text{ mJ/m}^2$  (e.g., 42.5 to 43.5), preferably greater than  $43.5 \text{ mJ/m}^2$ . The compositions alternatively or additionally advantageously provide films having a Polarity of from about 0.24 to about 0.31, preferably from about 0.245 to about 0.305, more preferably from about 0.25 to about 0.305, even more preferably from about 0.26 to about 0.30, most preferably from about 0.27 to about 0.29.

According to one embodiment of the present invention, the composition comprises a film-forming polymer and a suitable carrier comprising a volatile, organic solvent, and provides a film having a Surface Energy greater than 43.5 mJ/m<sup>2</sup>, preferably further having a Polarity of from about 0.24 to about 0.31.

According to another embodiment of the present invention, the composition comprises a polyurethane film-forming polymer and a suitable carrier comprising a volatile, organic solvent, and provides a film having a Surface Energy of from 42.5 to 43.5 mJ/m<sup>2</sup>, preferably further having a Polarity of from about 0.245 to about 0.305.

In another embodiment of the present invention, the composition comprises a cellulosic film-forming polymer, a polyurethane film-forming polymer and a suitable carrier comprising a volatile, organic solvent, and provides a film having a Polarity of from 0.245 to 0.305, preferably from 0.25 to 0.305, more preferably from about 0.26 to about 0.30, most preferably from about 0.27 to about 0.29.

Actual Surface Energy and Polarity are determined according to the following method.

The following symbols and terms are used in the method herein:

$\gamma_s = \gamma_s^d + \gamma_s^p$  for a test nail polish = surface energy of the test nail polish, wherein:

$\gamma_s^d$  = dispersive component of  $\gamma_s$

$\gamma_s^p$  = polar component of  $\gamma_s$

$x^p = \frac{\gamma_s^p}{\gamma_s}$  = polarity (equation 1)

Similarly,

$\gamma_L = \gamma_L^d + \gamma_L^p$  for a liquid = surface energy of the liquid, wherein:

$\gamma_L^d$  = dispersive component of  $\gamma_L$

$\gamma_L^p$  = polar component of  $\gamma_L$

Surface energy measurements are made using the Wilhelmy technique (described in A.W. Neumann and R.J. Good, Surface and Colloid Science, Vol. 2, R.J. Good and R.R. Stromberg, Eds., Plenum Press (1979)), a Krüss K12 tensiometer, and K121 software which is available from Krüss USA, Charlotte, NC (or equivalents thereof). All measurements are performed at 22 °C +/- 2 °C. In this

method, a platinum plate or a cover slip coated with a dried film of the test nail polish is suspended from a balance which measures weight in grams to ten thousandths of a gram. Each test liquid (separately, water and methylene iodide) has its own glass reservoir which is placed on top of a motorized platform allowing the test liquid to be brought into contact with the platinum plate or solid sample of interest, which is suspended from the balance overhead. The liquids are each introduced to a reservoir at a depth of about 1 cm.

To verify cleanliness of the reservoir and purity of the test liquid, the surface tension of each liquid in its respective reservoir is measured and checked versus literature values. With the platinum plate in place, the "Plate Method" is selected from the Krüss software. This method raises the platform until it determines the location of the plate-liquid interface (determined by the platform height at which the balance detects an increase of 0.001 gram). The platform then further raises 1 mm past this point, then returns to the height denoting the interface. At this point, one balance reading is taken each second for 10 seconds. The software displays the surface tension calculated by:

$$\gamma_L = \frac{F}{L_w \cos\theta} \quad (\text{equation 2})$$

wherein  $F$  = wetting force (measured by balance);  $L_w$  = wetted length (the perimeter of the plate); and  $\theta$  = contact angle (assigned a value of 0 for liquids against platinum).

Glass cover slips (thickness pre-measured using a digital vernier calipers to the nearest 0.01 mm, by taking the average of 5 measurements evenly distributed over the length of the slip) are attached to a level surface with Scotch® tape and the nail polish to be tested (test nail polish) is applied to one half of the top side of the cover slip in a similar manner to standard application of one layer of a nail polish composition to the nail (to form a smooth, essentially uniformly thick coat, about 40 microns in thickness once dried). The test nail polish is allowed to dry at ambient temperature for at least one hour. The cover slip is then turned over and once again attached to the level surface with Scotch® tape in such a manner that the polish does

not come in contact with any surface. The test nail polish is applied to the second side of the cover slip in a similar manner and allowed to dry at ambient temperature for at least one hour. The test nail polish is then further dried in a convection oven at 87°F for 24 hours. Six cover slips are prepared in the same manner for each  
5    polish to be tested. Measurements are taken on the prepared slips about 24 hours after application of the polish to the second side of the cover slip.

Once the slips and test liquids have been prepared as described above, the width and thickness of each nail polish film is measured using a digital vernier calipers to the nearest 0.01 mm. These measurements are used to determine the  
10    perimeter (P) (the "wetted length" in accordance with the nomenclature used by Krüss) according to the following equation:

$$P = (2 * \text{Width}) + (2 * \text{Thickness})$$

The width and thickness are inputs into the Krüss software, which performs calculation of the perimeter following the above formula.

15    A prepared slip is mounted in a holding clip and suspended from the balance. The Krüss software controlling the instrument raises the motorized platform holding the probe liquid reservoir (platform speed of 1.2 mm / min) until the balance detects a change in weight of 0.001 g. The height corresponding to this weight is denoted the interface height. The platform speed is then decreased to 60% of its original  
20    speed, and data collection (readings from the balance) is commenced. After raising the platform to 3 mm beyond the height of the interface such that the liquid contacts the film on the slip, the platform stops, waits one second, then reverses direction, collecting data throughout, until the sample pulls completely free of the probe liquid. The data collected as the platform rises is used to determine the advancing contact  
25    angle, while that data collected as the platform recedes is used to determine the receding contact angle. The software calculates both of these angles by performing a linear regression to each the "advancing" data and "receding" data plotted as force

vs. depth. The total force measured by the balance is a sum of the wetting force ( $F$  as given in equation (2) above) and the buoyancy force, which is a function of immersion depth. The buoyancy force is given by the slope of the linear regression and the wetting force is given by the y-intercept. Using the y-intercept and equation  
 5 (1), the advancing and receding contact angles are calculated. Advancing angles are always greater than or equal to receding angles. Advancing angles from measurements in both water and methylene iodide are used in determining the Surface Energy of the test nail polish film. Three of the six prepared slips for each nail polish are used to measure the contact angle of water on the film. The  
 10 remaining three prepared slips are used to measure the contact angle of methylene iodide on the film.

For each test nail polish, the three advancing water contact angle values are averaged, and the three methylene iodide advancing contact angle values are also averaged. These average contact angles for each of the two probe liquids are used to  
 15 determine the Surface Energy of the substrate.

Relation of interfacial tensions to contact angles is as follows:

$$\gamma_L \cos \theta = \gamma_S - \gamma_{SL}$$

where  $\gamma_{SL}$  = solid - liquid interfacial tension (equation 3)

and all others have the same definitions as given above.

The Harmonic Mean equation,

$$\gamma_{SL} = \gamma_S + \gamma_L - 4 \frac{\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} - 4 \frac{\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p}, \quad (\text{equation}$$

20 4)

provides a method for relating the solid-liquid interfacial tension to the individual solid and liquid surface energies and their dispersive and polar components (defined above). The equation used to calculate surface energies is obtained by combining equations (3) and (4), yielding:

$$\gamma_L \cos \theta = -\gamma_L + 4 \frac{\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} + 4 \frac{\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p}, \quad (\text{equation } 5)$$

Using equation 4, the known liquid surface tension as well as the dispersive and polar components for each probe liquid, and the experimentally determined contact angle, a system of 2 equations and 2 unknowns is obtained. Solving equations 4 and 5 simultaneously gives  $\gamma_S^d$  and  $\gamma_S^p$ , the dispersive and polar components of the test nail polish film's Surface Energy, respectively. These two values sum to give the total Surface Energy,  $\gamma_S$ . The Polarity,  $x^p$ , is calculated by equation (1), above.

Values used for liquid surface tension and its components for each test liquid are given in the table below:

| Test Liquid | $\gamma_L$ / mN / m | $\gamma_L^d$ / mN / m | $\gamma_L^p$ / mN / m |
|-------------|---------------------|-----------------------|-----------------------|
| water       | 72.3                | 18.7                  | 53.6                  |
| iodomethane | 50.8                | 48.5                  | 2.3                   |

#### Rheological Properties

The compositions hereof have rheological properties as defined by Yield Value and Plastic Viscosity. As will be understood by those skilled in the art, rheological properties are influenced by the level of solids and diluents present in the composition, including the level of any thickeners. For example, Plastic Viscosity tends to increase with increasing solid level, decreasing diluent level, and increasing thickener level. The Yield Value is preferably from about 0.3 Pascals ("Pa") to about 3.0 Pa, more preferably about 0.75 Pa to about 2.5 Pa. The Plastic Viscosity is preferably about 600 centipoise ("cP") or less, more preferably about 500 cP or less, even more preferably from about 200 cP to about 500 cP, most preferably from about 300 cP to about 450 cP. These rheological properties are measured using a controlled stress rheometer in a shear rate ramp. A Haake Model RS100 rheometer (or equivalent thereof) can be used, with a 60 mm parallel plate geometry set to operate with a 0.5 mm gap. Procedural details such as calibration, zero point

determination, gap setting, and filling sample volume are straightforward to one skilled in the art, and are guided by the RS100 software. A water bath cools the base plate to 20 degrees Celsius. The software is programmed in controlled rate mode to ramp shear rate from 0 to 300 inverse seconds over a 2 minute time period, and  
 5 collects 100 data points in that time. The data are modeled by the Casson equation, conveniently provided by the software. A linear regression of the square root of stress versus the square root of shear rate obtains the slope and intercept according to the equation:

$$\tau^{1/2} = \tau_0^{1/2} + \left( \eta_p \dot{\gamma} \right)^{1/2}$$

10 Where:

$\tau$  = stress (measured, Pa)

$\dot{\gamma}$  = shear rate (measured, 1/seconds)

$\tau_0$  = Yield Value (calculated by regression)

$\eta_p$  = Plastic Viscosity (calculated by regression)

#### 15 Mechanical Properties

The compositions hereof can be further characterized by providing films having a Young's Modulus (at time<sub>test</sub> = 24 hours) of about 450 MPa or more, more preferably about 550 MPa or more, most preferably about 750 MPa or more. Compositions having these mechanical properties tend to provide further improved  
 20 wear properties.

It has been found that the Young's Modulus is a function of the type and level of cellulosic film forming polymer, polyurethane film forming polymer, and/or non-epoxy containing plasticizer in the composition. Preferred compositions have a Young's Modulus predicted by the following equation:

$$\begin{aligned} & \text{25 } \text{Young's Modulus (predicted) (MPa)} = \\ & (207)(\text{wt \% cellulosic polymer}) - (241)(\text{wt\% non-epoxy plasticizer}) \end{aligned}$$

Actual Young's Modulus of the present compositions is determined in the following manner:

(a) Sample preparation:

The nail polish to be tested is drawn down on a flat surface (e.g. a 10 inch x 11 inch glass plate) covered with a double layer of Teflon® sheet (e.g., Bytac VF-81, commercially available from Norton Performance Plastics Corporation of Akron, Ohio). An abrasive emery board is used to scratch the Teflon® surface lightly on the

Young's Modulus is determined by tensile testing of strips of the nail polish film as follows:

10 (a) Sample preparation:

The nail polish to be tested is drawn down on a flat surface (e.g. a 10 inch x 11 inch glass plate) covered with a double layer of Teflon® sheet (e.g., Bytac VF-81, commercially available from Norton Performance Plastics Corporation of Akron, Ohio). An abrasive emery board is used to scratch the Teflon® surface lightly on the  
15 sides, outlining a rectangular draw down area so the wet sample adheres temporarily to the Teflon® sheet while it dries (the rectangular draw down area is defined by long sides approximately the inside width of a drawdown bar and both ends). Using a 6.0 mil bird applicator draw down bar, draw down a nail polish wet film. The bird applicator bar draws a 3 inch wide coating of polish and the overall length of the bar  
20 is 4.5 inches. Such wet film applicators are available from coatings test equipment suppliers such as the Paul N. Gardner Company, Inc., Pompano Beach, Florida. Place the coated substrate in a 87 °F convection oven for five minutes.

After five minutes of drying to give a first film, remove from the oven and clean the perimeter of the drawdown area by gently scraping away excess film from  
25 the edge with a spatula. Draw down a second coat of the same polish directly on the first film, again using the 6 mil draw down bar. Then place the coated substrate in the 87 °F convection oven for 40 minutes.

After 40 minutes of drying remove the coated substrate from the oven, remove the films from the substrate and cut them into 1/2 inch wide strips using a

precision film strip cutter such as a JDC Precision Sample Cutter (available from Paul N. Gardner Company, Inc. of Pompano Beach, Fla.) (or equivalent thereof which ensures the edges are the same width across the whole sample length, and smooth so as not to start a tear or other flaw/weak point in the film). Place the strips  
5 on a Teflon<sup>®</sup> covered plate pushing down gently to make good contact with the Teflon<sup>®</sup>. The strips are then returned to the 87 °F convection oven until they are required for testing. Mechanical properties are tested at 24 hours (time 0 [ $t_0$ ] being the time at which the second drawdown is completed and the sample replaced into the oven to dry the second layer, time  $t_{test}$  being the time after  $t_0$  at which the  
10 mechanical properties are tested).

For testing the mechanical properties, remove a strip from the oven and cut into 2.25 inch lengths using the JDC Precision Sample Cutter or equivalent. Affix a 1 inch piece of Scotch brand tape to each end of the strip (approximately 0.125" into the sample) and fold it over on itself to produce half inch "taped ends" with a non-  
15 taped sample length of 2 inches. Measure the thickness of the film strip to be tested using a micrometer (e.g. Mitutoyo micrometer). The thickness is measured to the nearest 0.001 mm by averaging the thickness of 5 spots evenly distributed along the length of the film. If the average measured film thickness is between 0.04 and 0.05 mm then proceed with the test. If not, modify the drawdown procedure given above  
20 for the nail polish being tested in order to bring its dry film thickness to within the 0.04 to 0.05 mm range (i.e., additional coats can be applied if the film is too thin; fewer coats and/or a 3 mil draw-down bar may be substituted if the film is too thick)

(b) Testing:

The mechanical properties of the film strips are measured on a calibrated  
25 Instron 4500 series apparatus (or equivalent thereof) using Instron Series IX software for Windows (Merlin version) (or equivalent thereof). Both the equipment and software are commercially available from Instron Corp., Canton, MA. In the test, the Instron measures the force as a function of applied tensile strain. A 100 N static

load cell, a 2.0 inch gauge length, at a crosshead speed of not less than 2 and not greater than 20 inches travel/minute is used. Pneumatic action jaws at a minimum 40 PSI air pressure are used with 1 inch x 0.5 inch smooth rubber coated faces to hold the test film (available from Instron Corp., Canton, MA).

5       The Series IX software is automatically programmed to report strain (mm/mm), Young's modulus (MPa) and toughness (MPa). "Strain" is measured as film elongation (mm/mm) to break; "Young's modulus" is the initial slope of the stress/strain curve; "toughness" is measured as the area under the stress/strain curve to break, which is equal to the energy to break divided by the sample volume,  
10       reported elsewhere in various units such as kg<sub>f</sub>mm/mm<sup>3</sup> or also psi.

      The Instron is calibrated and checked at the start of the experiment with dead weights to ensure accuracy. Appropriate data for the film (for example, thickness, width, gauge length, and sample number) are entered into the computer and a film strip is loaded into the grips, being careful not to damage the film while loading,  
15       especially at the grips. The taped ends of the film are used to provide a reinforcement for the part of the film within the grips. Avoid direct contact with the films to eliminate possible contamination from skin oils which may influence results. In order to present a film exactly parallel to the direction of the pull, with no wrinkles, use of a simple guide may be necessary.

20       Begin the tensile test and run until the film breaks. Watch the film during the run to ensure the film does not break at the grips or at a film flaw. If either of these occur, discard the data for that strip. Repeat the process for all film strips. At least six sample pulls are obtained for each nail polish sample, more if needed to develop a reproducible, average result (the Young's Modulus should have a standard error of  
25       the mean of less than about 5%). The average break strain, Young's Modulus and toughness of the film to break are calculated from all of the samples for each time point of interest, and reported as the % Strain (mm/mm), Young's Modulus (MPa), and Toughness Value (MPa).

Equivalents to the above described hardware/software must be thoroughly evaluated because there are many known differences from machine to machine. In order to ensure reproducibility of results from machine to machine, a standard plastic test strip is run to ensure both hardware and software are working according to specifications. Polyethylene bags measuring 6" x 8" x 0.002" by Loc-Top,  
5 (commercially available as Catalog No. ML-68NC from ResourceNet, Cincinnati, OH) (or equivalent thereof), are used as a standard plastic test film for tensile tests. These are cut into 1/2 inch strips cutting parallel to the top opening. The strips are run at a length of 6 inches (*i.e.*, not cut to size); gauge length remains 2 inches. The  
10 sample is loaded and tested as above. Table I below shows typical results for the plastic strips.

Table I

| Parameter                | Result                |
|--------------------------|-----------------------|
| Thickness                | 0.0395 mm (+/- 2%)    |
| Peak Stress              | 29.8 MPa (+/- 5%)     |
| Maximum Strain           | 2.1 mm/mm (+/- 5%)    |
| Young's Modulus          | 238 MPa (+/- 3%)      |
| Toughness Value at Break | 48.2 MPa (+/- 11%)    |
| Cross-head Speed         | 2 to 20 inches/minute |

### Examples

The following examples further describe and demonstrate embodiments  
15 within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention.

In the examples below, all polymer component percentages are expressed in  
20 weight percent of solid polymer (based on the total composition).

The compositions of Examples 1-19 are suitable for use as nail polish compositions.

| Ingredient                   | Example 1 | Example 2 | Example 3 | Example 4 |
|------------------------------|-----------|-----------|-----------|-----------|
| Solid NC 1/4"                | 15.4      | 15.4      | 15.4      | 13.3      |
| Solid Sanres EX 499          | 2         | 2         | 2         | 2.85      |
| Solid Epoxy E-75             | 1.195     | 1.195     | 1.195     | 1.195     |
| Uniplex 670P                 | 0         | 0         | 0         | 0.999     |
| Uniplex PX45                 | 6         | 6         | 6         | 4         |
| Clay/bentonite/ hectorite    | 1.2       | 1.2       | 1.2       | 1.2       |
| Red #7 lake                  | 0.555     | 0.007     | 0.182     | 0.555     |
| Red #6 lake                  | 0.485     | 0.099     | 0.087     | 0.485     |
| Yellow #5 lake               | 0         | 0.038     | 0         | 0         |
| TiO <sub>2</sub>             | 0.13      | 0.884     | 0         | 0.13      |
| Red Iron Oxide               | 0.104     | 0.215     | 0         | 0.104     |
| Black Iron Oxide             | 0.026     | 0.059     | 0.017     | 0.026     |
| Mica Pearl (Flamenco Velvet) | 0         | 0         | 1.014     | 0         |
| Butyl acetate                | 32.863    | 32.863    | 32.863    | 33.573    |
| Ethyl acetate                | 27.386    | 27.386    | 27.386    | 27.977    |
| Isopropyl alcohol            | 10        | 10        | 10        | 9.15      |
| Benzophenone                 | 0.026     | 0.013     | 0.007     | 0.026     |
| Camphor                      | 1         | 1         | 1         | 1         |
| Propyl Acetate               | 0.042     | 0.112     | 0.027     | 0.042     |
| Paraplex G-50                | 1         | 1.035     | 1.478     | 2.8       |
| Dibutyl phthalate            | 0.589     | 0.497     | 0.144     | 0.589     |

| Ingredient                   | Example 5 | Example 6 | Example 7 | Example 8 |
|------------------------------|-----------|-----------|-----------|-----------|
| Solid NC 1/4"                | 13.3      | 13.3      | 15.3      | 15.3      |
| Solid Sanres EX 499          | 2.85      | 2.85      | 2.5       | 2.5       |
| Solid Epoxy E-75             | 1.195     | 1.195     | 1.011     | 1.011     |
| Uniplex 670P                 | 0.999     | 0.999     | 0.9       | 0.9       |
| Uniplex PX45                 | 4         | 4         | 5.5       | 5.5       |
| Clay/bentonite/ hectorite    | 1.2       | 1.2       | 1.1       | 1.1       |
| Red #7 lake                  | 0.007     | 0.182     | 0.47      | 0.006     |
| Red #6 lake                  | 0.099     | 0.087     | 0.41      | 0.084     |
| Yellow #5 lake               | 0.038     | 0         | 0         | 0.032     |
| TiO <sub>2</sub>             | 0.884     | 0         | 0.11      | 0.748     |
| Red Iron Oxide               | 0.215     | 0         | 0.088     | 0.182     |
| Black Iron Oxide             | 0.059     | 0.017     | 0.022     | 0.05      |
| Mica Pearl (Flamenco Velvet) | 0         | 1.014     | 0         | 0         |
| Butyl acetate                | 33.573    | 33.573    | 32.473    | 32.473    |
| Ethyl acetate                | 27.977    | 27.977    | 27.061    | 27.061    |

|                   |       |       |       |       |
|-------------------|-------|-------|-------|-------|
| Isopropyl alcohol | 9.15  | 9.15  | 10    | 10    |
| Benzophenone      | 0.013 | 0.007 | 0.022 | 0.011 |
| Camphor           | 1     | 1     | 1     | 1     |
| Propyl Acetate    | 0.112 | 0.027 | 0.035 | 0.095 |
| Paraplex G-50     | 2.834 | 3.278 | 1.5   | 1.529 |
| Dibutyl phthalate | 0.497 | 0.144 | 0.498 | 0.42  |

| Ingredient                   | Example 9 | Example 10 | Example 11 | Example 12 |
|------------------------------|-----------|------------|------------|------------|
| Solid NC 1/4"                | 15.3      | 15.15      | 15.15      | 15.15      |
| Solid Sanres EX 499          | 2.5       | 2.35       | 2.35       | 2.35       |
| Solid Epoxy E-75             | 1.011     | 1.103      | 1.103      | 1.103      |
| Solid Uniplex 670P           | 0.9       | 1          | 1          | 1          |
| Solid Uniplex PX45           | 5.5       | 5.2        | 5.2        | 5.2        |
| Clay/bentonite/ hectorite    | 1.1       | 1.2        | 1.2        | 1.2        |
| Red #7 lake                  | 0.154     | 0.512      | 0.006      | 0.168      |
| Red #6 lake                  | 0.074     | 0.448      | 0.091      | 0.08       |
| Yellow #5 lake               | 0         | 0          | 0.035      | 0          |
| TiO <sub>2</sub>             | 0         | 0.12       | 0.816      | 0          |
| Red Iron Oxide               | 0         | 0.096      | 0.198      | 0          |
| Black Iron Oxide             | 0.014     | 0.024      | 0.054      | 0.016      |
| Mica Pearl (Flamenco Velvet) | 0.858     | 0          | 0          | 0.936      |
| Butyl acetate                | 32.473    | 32.832     | 32.832     | 32.832     |
| Ethyl acetate                | 27.061    | 27.36      | 27.36      | 27.36      |
| Isopropyl alcohol            | 10        | 10         | 10         | 10         |
| Benzophenone                 | 0.006     | 0.024      | 0.012      | 0.007      |
| Camphor                      | 1         | 1          | 1          | 1          |
| Propyl Acetate               | 0.023     | 0.038      | 0.104      | 0.025      |
| Paraplex G-50                | 1.905     | 1          | 1.032      | 1.441      |
| Dibutyl phthalate            | 0.122     | 0.543      | 0.458      | 0.133      |

#### Preparation of pigment slurries:

The mixtures should only be prepared under the direction of experienced operators who have been trained in safe practices for milling or otherwise mixing volatile solvents. Use only safely installed, wired, ventilated, temperature controlled and monitored equipment.

Blend the solvent, nitrocellulose and plasticizer together at room temperature or below until homogeneous by combining in a jar or other suitable container a portion of nitrocellulose (about 1/3 of the nitrocellulose needed to prepare a batch of nail polish), a portion of the total plasticizer (about one half the plasticizer), and sufficient solvent to reduce the viscosity to less than about 1,000 cP (about 50-75%

of the available solvent) and shaking on a paint shaker until homogeneous, about ½ hour. An industrial paint shaker such as are commonly used to shake paint cans can be used (available from Paul N. Gardner Company, Inc. of Pompano Beach, Florida). To allow for any material losses during processing or for making a master  
5 batch, an excess of ingredients can be used to prepare the slurry.

Add all the dry pigment, excluding the mica if present, and clay to the container and shake for about ½ hour to wet the pigment and clay. Transfer the mixture to a high shear mixer such as a MiniZeta 03 mill (manufactured by Netzsch of Germany, employing about 300 ml of 0.6-1 mm Yttrium-Doped Zirconium beads  
10 (or an equivalent). The mill is preferably powered by an air compressor or house air supplying about 100-120 psi. The milling chamber and shaft should be cooled to below 20°C prior to and during milling, e.g., using a suitable re-circulating cooling bath set to cool to between 0°C and -10°C. Mill until the average particle size is less than about 5 microns, determined using a A Horiba LA-910 particle size analyzer  
15 equipped with a fraction cell holder and cell (available from Horiba, Ltd, Irvine CA, USA). Transfer the slurry to a jar or other suitable container and store until needed for preparation of a nail polish.

Suitable pigment slurries are typically, alternatively prepared by a pigment supplier as a raw material for sale to the cosmetics industry. One such supplier is  
20 Kirker Enterprises, Inc. of Paterson, NJ. The pigment slurries contain the ground (i.e., milled) pigment in solvent with clay, nitrocellulose polymer and plasticizer, the pigment being ground to a particle size of about 1-10 microns average.

#### Preparation of nail polish:

Combine the balance of the solvent, plasticizer, mica and other nail polish  
25 ingredients exclusive of the pigment/clay slurry in a jar or other suitable container. Add an appropriate amount (formula proportion) of the pigment slurry to this mixture. Seal and shake the container on a paint shaker for about 30 minutes. Package in suitable storage containers, e.g., small nail polish bottles, at or below room temperature.

| Ingredient  | Example 13 | Example 14 | Example 15 |
|-------------|------------|------------|------------|
| Solid NC ¼" | 15.15      | 15.15      | 15.15      |

|  |        |        |        |
|--|--------|--------|--------|
| Solid Sanres EX 499                      | 2.35   | 2.35   | 2.35   |
| Solid Epoxy E-75                         | 1.103  | 1.103  | 1.103  |
| Uniplex 670P                             | 1      | 1      | 1      |
| Uniplex PX45                             | 5.2    | 5.2    | 5.2    |
| Clay/bentonite/hectorite                 | 1.2    | 1.2    | 1.2    |
| Red #7 lake (Soft-tex) <sup>1</sup>      | 0.512  | 0.006  | 0.168  |
| Red #6 lake (Soft-tex) <sup>1</sup>      | 0.448  | 0.091  | 0.08   |
| Yellow #5 lake (Soft-tex) <sup>1</sup>   | 0      | 0.035  | 0      |
| TiO <sub>2</sub> lake                    | 0.12   | 0.816  | 0      |
| Red Iron Oxide (Soft-tex) <sup>1</sup>   | 0.096  | 0.198  | 0      |
| Black Iron Oxide (Soft-tex) <sup>1</sup> | 0.024  | 0.054  | 0.016  |
| Mica Pearl (Flamenco Velvet)             | 0      | 0      | 0.936  |
| Butyl acetate                            | 32.832 | 32.832 | 32.832 |
| Ethyl acetate                            | 27.36  | 27.36  | 27.36  |
| Isopropyl alcohol                        | 10     | 10     | 10     |
| Benzophenone                             | 0      | 0      | 0      |
| Camphor                                  | 1      | 1      | 1      |
| Paraplex G-50                            | 1.062  | 1.147  | 1.473  |
| Dibutyl phthalate                        | 0.543  | 0.458  | 0.133  |

<sup>1</sup> Sun Chemical, primary particle size about 20 nm to about 200 nm by microscopic particle size analysis

#### Preparation of nail polish:

The mixtures should only be prepared under the direction of experienced operators who have been trained in safe practices for milling or otherwise mixing volatile solvents. Use only safely installed, wired, ventilated, temperature controlled and monitored equipment.

Blend all materials except the pigment and clay together at room temperature or below until homogeneous by combining in a jar or other suitable container and shaking on a paint shaker until homogeneous, about ½ hour. An industrial paint shaker such as are commonly used to shake paint cans can be used (available from Paul N. Gardner Company, Inc. of Pompano Beach, Florida).

Weigh an excess of pigments, excluding mica, in proper proportion and dry mix in an Osterizer food blender or equivalent about 1 minute until homogeneously mixed. Add this blended mixture to a Model 0 jet mill manufactured by Fluid Energy AJet of Plumsteadville, PA, USA. Use compressed nitrogen as the fluid gas

and set the grinding nozzles to 100 psi, the feed nozzle to 85 psi, and the vibration-feeding device to a feed rate of 30-40 on the Model-O dial. The feed rate is about 100 g per hour. Jet mill and collect the pigments.

Add the correct amount of jet milled pigment blend and clay to the liquid  
 5 ingredient mix and shake for ½ hour on paint shaker. Transfer the mixture to a high shear mixer such as a MiniZeta 03 mill (manufactured by Netzsch of Germany, employing about 300 ml of 0.6-1 mm Yttrium-Doped Zirconium beads). The mill is powered by an air compressor or house air supplying about 100-120 psi. The milling chamber and shaft are cooled to below 20°C prior to and during milling,  
 10 using a re-circulating cooling bath set to cool to between 0°C and -10°C. Mill until 99% of the particles are less than 1 micron diameter, determined using a Horiba LA-910 particle size analyzer equipped with a fraction cell holder and cell (available from Horiba, Ltd, Irvine CA, USA).

Add the mica in proportion and wet mill just until dispersed, for a period less  
 15 than 10 minutes. Viscosity can be adjusted, e.g., by adding more clay (such as milled in solvents at ca. 4%-8% clay solids) (to increase viscosity), or by adding more solvent (to lower viscosity), followed by paint shaking to blend. Package in suitable storage containers, e.g., small nail polish bottles, at or below room temperature.

20 The above compositions are independently contiguously applied to human fingernails using a standard brush-applicator. A nail polish layer is allowed to form by drying under ambient conditions for a period of five minutes. Then a second layer is applied. The nail polish is allowed to dry for at least several minutes to form a wear-resistant film.

25

| Ingredient                            | Example 16 | Example 17 | Example 18 | Example 19 |
|---------------------------------------|------------|------------|------------|------------|
| Solid NC 1/4"                         | 15.0       | 13.0       | 12.0       | 11.0       |
| Solid Sanres EX519                    | 2.0        | 4.0        | 5.5        | 7.0        |
| Epoxy NX-55                           | 1.1        | 1.6        | 3.1        | 1.6        |
| Avalure AC315                         | 3.0        | 2.5        | 1.5        | 3.0        |
| Uniplex PX45                          | 5.5        | 4.5        | 5.5        | 4.0        |
| Clay/bentonite/hectorite              | 1.2        | 1.2        | 1.2        | 1.2        |
| Red #7 solid (Soft-tex) <sup>1</sup>  | 0.156      | 0.156      | 0.156      | 0.156      |
| Red #34 solid (Soft-tex) <sup>1</sup> | 0.031      | 0.031      | 0.031      | 0.031      |

|   |       |       |       |       |
|---|-------|-------|-------|-------|
| TiO <sub>2</sub> solid                            | 0.281 | 0.281 | 0.281 | 0.281 |
| Red Iron Oxide solid<br>(Soft-tex) <sup>1</sup>   | 0.460 | 0.460 | 0.460 | 0.460 |
| Black Iron Oxide solid<br>(Soft-tex) <sup>1</sup> | 0.229 | 0.229 | 0.229 | 0.229 |
| Buryl Acetate                                     | 29.7  | 30.3  | 30.0  | 29.7  |
| Ethyl Acetate                                     | 24.8  | 25.2  | 25.0  | 24.8  |
| Isopropyl Acetate                                 | 15.0  | 15.0  | 15.0  | 15.0  |
| Paraplex G-50                                     | 1.5   | 1.5   | 0.0   | 1.5   |

<sup>1</sup> Sun Chemical, primary particle size about 20 nm to about 200 nm by microscopic particle size analysis

Nail polishes of Examples 16-19 are prepared in the manner described for Examples 1-12 or 13-15.

## WHAT IS CLAIMED IS:

1. A nail polish composition comprising:
  - (a) a film-forming polymer; and
  - (b) a carrier comprising a volatile, organic solvent suitable for application to the nails;characterized in that the composition is solvent-borne and provides a film having a Surface Energy of greater than  $43.5 \text{ mJ/m}^2$ .
2. A nail polish composition comprising:
  - (a) a film-forming polyurethane; and
  - (b) a carrier comprising a volatile, organic solvent suitable for application to the nails;characterized in that the composition is solvent-borne and provides a film having a Surface Energy of from  $42.5$  to  $43.5 \text{ mJ/m}^2$  and a Polarity of from  $0.245$  to  $0.305$ .
3. A nail polish composition comprising:
  - (a) a film-forming cellulosic polymer;
  - (b) a film-forming polyurethane; and
  - (c) a carrier comprising a volatile, organic solvent suitable for application to the nails;characterized in that the composition is solvent-borne and provides a film having a Polarity of from  $0.245$  to  $0.305$ .
4. The composition of Claim 1, characterized in that the composition comprises a film-forming polyurethane and a film-forming cellulosic polymer.
5. The composition of Claim 1 or 4 characterized in that the composition provides a film further having a Polarity of from  $0.24$  to  $0.31$ .
6. The composition of Claim 2 characterized in that the composition further comprises a film-forming cellulosic polymer.

7. The composition of Claim 3 characterized in that the Polarity is from 0.26 to 0.30, preferably from 0.27 to 0.29.
8. The composition of any of Claims 2-7, characterized in that the composition comprises at least 1.5% film-forming polyurethane.
9. The composition of any of the preceding claims, characterized in that the composition has a Plastic Viscosity of 600 cP or less, preferably 300 cP to 450 cP.
10. The composition of any of the preceding claims, characterized in that the composition provides a film further having a Young's Modulus of 450 MPa or more, preferably 550 MPa or more, more preferably 750 MPa or more, at time<sub>test</sub> = 24 hours.
11. The composition of any of the preceding claims characterized in that the composition is essentially free of formaldehyde resin.

# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/IB 99/00646

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 A61K7/043

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages               | Relevant to claim No. |
|------------|--|-----------------------|
| A          | US 5 676 935 A (DE LA POTERIE VALERIE ET AL) 14 October 1997 (1997-10-14)<br>tables 1,2<br>----- |                       |
| A          | US 5 290 543 A (OUNANIAN HOVIG ET AL) 1 March 1994 (1994-03-01)<br>claim 3<br>-----              |                       |
| A          | EP 0 593 959 A (HUETTENES ALBERTUS) 27 April 1994 (1994-04-27)<br>claims 1-4; example 4<br>----- |                       |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" documents referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

30 July 1999

Date of mailing of the international search report

06/08/1999

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Information on patent family members

International Application No

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